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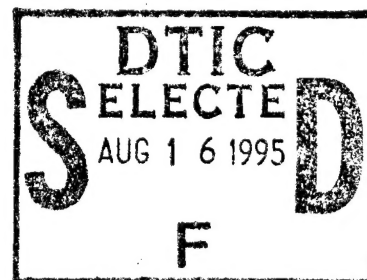
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UNITED STATES ATOMIC ENERGY COMMISSION

A STUDY OF THE SEPARATION OF HAFNIUM AND ZIRCONIUM USING TTA

By
Dorothy C. McCarty
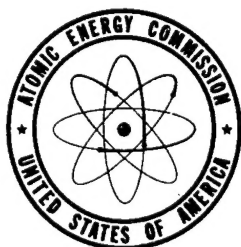Burton E. Dearing
John F. Flagg

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Knolls Atomic Power Laboratory
Schenectady, New York

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GENERAL ELECTRIC COMPANY

KNOLLS ATOMIC POWER LABORATORY

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The two-phase equilibrium of Zr^{+4} between a dilute acid aqueous phase and
the thenoyltrifluroacetone (TTA) chelate of zirconium in benzene was investi-
gated by R. E. Connick and W. H. McVey UCRL-101 (AECD-2272). Their studies
were essentially all done in perchloric acid and gave information on the
principal species of zirconium found in the aqueous phase, the species extract-
ing into the benzene and equilibrium constants for the reaction in $2\underline{M}$ $HClO_4$.
In addition they investigated the effect on the extraction coefficients of
various substances known to complex zirconium in aqueous solution, in
particular bisulphate and fluoride ions.

It was the purpose of the present work to investigate a hafnium system
in a similar manner and compare the results with a possible view toward
developing a zirconium-hafnium separation. A nitric acid system has been used
for the majority of this work, but, as will be shown later, the data can be
compared with perchloric acid systems by making a correction for nitrate
complexing in the aqueous phase.

The work reported here covers a study of (a) both hydrogen and TTA
power dependencies in the hafnium extraction, (b) complexing of hafnium by
sulfate, nitrate, oxalate, and chloride ions, (c) rate phenomena in both the
hafnium and zirconium systems, and (d) separation of hafnium and zirconium in
mixtures. In addition, some of the published data on the zirconium extraction
has been rechecked. The experimental work on pure hafnium solutions is
described first, followed by experiments on zirconium, and finally by work
on separations.

PART I HAFNIUM

EXPERIMENTAL

Method and Materials

The method consisted of contacting an aqueous phase with a benzene phase containing TTA. The preparation and properties of this reagent have been adequately described elsewhere (AECD-2272, BC-63, AECD-1405).

At low TTA concentrations the metal ion is presumably uncomplexed in the aqueous phase but forms a chelate compound which, being soluble in the organic phase, extracts. The equilibrium thus established between the chelated form and the aqueous species can be measured by tracer techniques.

The TTA has a distribution coefficient of 40 between benzene and dilute hydrochloric acid at room temperature. This coefficient increases with increasing concentration of TTA mainly due to dimerization in the benzene phase. To make corrections for these changes, activity coefficients for TTA in benzene were reported by E. L. King and W. H. Reas (BC-69, July, 1947). These coefficients were used in the work reported here.

Weighed amounts of TTA were dissolved in thiophene-free benzene to give solutions of the desired concentrations. An additional check on the concentration was obtained by titration of aliquots of the benzene solutions with sodium hydroxide to the phenolphthalein end point.

The experiments were carried out with a concentration of hafnium of the order of $10^{-5}\underline{M}$. The tracer Hf^{181} was obtained from Dr. J. Ayres in HCl solution having been prepared in the following manner: Pure HfO_2 was bombarded in such a way that the cross-section for active zirconium, if present, was

only 1% of the cross-section for active hafnium production. The irradiated powder was dissolved in HF, fumed with H_2SO_4 to remove HF, precipitated with ammonia, washed to remove sulphate, and finally redissolved in HCl to form the stock solution.

An absorption curve on portions of this resulting stock solution gave a curve comparing favorably with that for pure Hf^{181} (Voigt and Thamer, AECD-2083). The activity, obtained in HCl solution, was converted to HNO_3 solution for most runs. In other runs the activity was extracted directly into TTA-benzene from the HCl solution and this benzene then used as a stock solution for the activity. In many experiments the equilbria were established from both directions and good agreement was always found.

The solutions were mixed in a vessel as shown (Fig. 1) and stirred for 2 hours to insure equilibrium. In most of the experiments an ionic strength of 2 was maintained by HNO_3- $NaNO_3$ mixtures. Each phase was analyzed by mounting samples (usually .100 - .150 ml) on 25 mm watch glasses and evaporating under a heat lamp. The watch glasses were placed on cupped aluminum plates, covered with very thin cellophane, and counted. Since, in most cases of low acidity, an appreciable amount of salt remained on the plate, a calibration curve was required to correct any absorption effect of the salt.

Absorption Effect in Counting Aqueous Samples

It is often observed in fission product counting (beta-gamma) that an increase in counting rate is obtained when a precipitate is present on the

counting plate. The maximum may be reached at 15-20 mg after which the amount falls off as the self-absorption becomes more important than back-scattering.

To find the effect of $NaNO_3$ on the hafnium counts, a series of experiments was made in which hafnium tracer activity on the counting plates was compared with an equal aliquot of activity mixed with varying amounts of $NaNO_3$. The results are shown in Figure 2. These gave a correction factor which could be applied to the data in calculating distribution ratios. This factor is positive, in contrast with activities having a much harder beta.

RESULTS

Acid Power Dependence

The hafnium system was first investigated as a function of acidity. The TTA concentration was held constant at .02$\underline{M}$ while the acid was varied from about .5$\underline{M}$ to over 3$\underline{M}$ H$^+$. The ionic strength of each solution was maintained constant at 2 by suitable mixtures of $NaNO_3$ and HNO_3 (except for the one point at 3.3$\underline{N}$ H$^+$). In all cases the correction for absorption in the aqueous samples was applied. Acidities were determined by titration at the end of a run.

Each run was stirred for 2 hours to insure equilibrium. Time data initially taken indicated 80-90 minutes were required to reach equilibrium. The 2 hour period should be ample for reaching equilibrium regardless of the conditions used.

The results are given in Table I.

TABLE I

Extraction of Hafnium at Varying Acidity
TTA : .02$\underline{M}$

H^+ $\underline{N}$	Log H^+	$E\frac{b}{a}$	Log E
.297	-0.526	76.43	1.884
.155	- .809	176.75	2.248
.101	- .995	180.31	2.257
.0734	-1.134	103.65	2.016
.151	- .820	213.69	2.330
.983	- .006	2.423	0.385
.464	- .333	27.213	1.436
.661	- .179	9.127	0.961
.325	- .487	66.33	1.822
1.185	$+$ .074	1.568	0.196
1.896	$+$ .278	.207	-0.683
1.99	$+$ .300	.1524	-0.816
1.97	$+$ .295	.222	-0.653
3.32	$+$ .522	.05	-1.3
1.02	$+$ .009	2.456	0.390

These data (Figure 3) then indicate rather well that the acid power dependence does change with acid concentration and, in fact, that the species extracting must change. The points at very low acidities are not reproducible. As with zirconium, radio-colloids probably begin to form and this could explain the low values of E found. At 2$\underline{M}$ HNO$_3$ the slope can easily be 4 which is in line with the corresponding data on TTA power dependence at 2$\underline{M}$ HClO$_4$. Thus:

$$Hf^{+4} + 4\ HK \rightleftharpoons HfK_4 + 4\ H^+$$
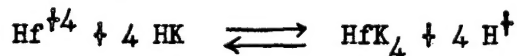
However, at lower acidities, 1$\underline{M}$ or less the slope is definitely 3 (with, as will be seen, a corresponding TTA dependence of 2). Such a system might be as follows:

$$Hf\ (OH)^{+3} + 2\ HK \rightleftharpoons HfOK_2 + 3\ H^+$$

Just where the transitions occur cannot be definitely stated for the change must be gradual. It is perfectly conceivable that the two species postulated above could be competing and, depending on the acidity of the system, one or the other form is favored. As will be seen later in the section on TTA power dependence, the actual data do not give a value of 4 but rather somewhat less than 4. This could be anticipated if two species, one involving 4 HK and the other 2 HK, are present.

TTA Power Dependence

The dependence of the extraction coefficient was next investigated as a function of TTA concentration. At constant acidity, the TTA was varied over the range .01 to 0.10$\underline{M}$. The best slope through the $2\underline{M}$ H^+ data indicates the power dependence is approaching 4. With that in mind a series of experiments was run at $3.32\underline{M}$ H^+ to see if the slope actually was approaching, or had, reached 4. These data together with those at $1\underline{M}$ H^+ are given in Tables II-V.

TABLE II

Extraction of Hafnium at Varying TTA Concentration

1.96$\underline{N}$ H^+ (HNO$_3$) $\mu = 2$
S = 3.47   Figure 4

TTA	Activity Coeff. TTA	Log (TTA)	$E\frac{b}{a}$	Log E
.02	.980	-1.704	.222	- .653
.03	.981	-1.530	1.09	.039
.04	.974	-1.409	2.70	.432
.06	.957	-1.240	11.07	1.044
.08	.943	-1.122	15.4	1.189
.10	.930	-1.031	59.8	1.78

TABLE III

Extraction of Hafnium at Varying TTA Concentration

3.32$\underline{N}$ H$^+$ (HNO$_3$) μ = 3.3

S = 3.77   Figure 5

TTA	Activity Coeff. TTA	Log (TTA)	$E\frac{b}{a}$	Log E
.04	.974	-1.409	.523	- .281
.06	.957	-1.240	2.16	.336
.08	.943	-1.122	5.78	.762
.10	.930	-1.031	13.84	1.142

TABLE IV

Extraction of Hafnium at Varying TTA Concentration

1.02$\underline{N}$ H$^+$ (HNO$_3$-NaNO$_3$) μ = 2

S = 2 or 3   Figure 6

TTA	Activity Coeff. TTA	Log (TTA)	$E\frac{b}{a}$	Log E
.005	.999	-2.301	.038	-1.42
.01	.996	-2.001	.317	- .498
.02	.988	-1.704	2.46	0.390
.04	.974	-1.409	11.9	1.078
.05	.965	-1.316	17.2	1.236
.08	.943	-1.122	26.4	1.422
.08	.943	-1.122	24.4	1.387
.10	.930	-1.031	71.3	1.854

TABLE V

Extraction of Hafnium at Varying TTA Concentration

2.0$\underline{M}$ H$^+$ (HClO$_4$) μ = 2

S = 3 or 4   Figure 7

TTA	Activity Coeff. TTA	Log (TTA)	$E\frac{b}{a}$	Log E
.02	.988	-1.704	.450	- .346
.04	.974	-1.409	6.0	.779
.10	.930	-1.031	60.9	1.786
.10	.930	-1.031	118.2	2.074

Before it seemed advantageous to work at constant ionic strength of 2, a series of experiments was made at ~0.5$\underline{N}$ and ~0.9$\underline{N}$ HNO$_3$. While these experiments cannot be readily correlated with subsequent runs, they are here reported for the sake of completeness. The runs are consistent in themselves since in each the acid is constant while the TTA concentration varies.

TABLE VI

Extraction of Hafnium at Varying TTA Concentration

.457$\underline{N}$ H$^+$ (HNO$_3$)   Figure 8
S = 1.94

TTA	Activity Coeff. TTA	Log TTA	E$\frac{b}{a}$	Log E
.015	.993	-1.826	3.89	.591
.01	.996	-2.001	2.15	.333
.01	.996	-2.001	1.82	.260
.02	.988	-1.704	5.58	.747
.02	.988	-1.704	7.94	.901
.02	.988	-1.704	6.45	.810
.03	.981	-1.530	17.06	1.233
.04	.974	-1.409	24.25	1.386
.06	.957	-1.240	108.8	2.037
.08	.943	-1.122	182.7	2.262

TABLE VII

Extraction of Hafnium at Varying TTA Concentration

.916$\underline{N}$ H$^+$ (HNO3)
S = 2.3 - 2.5   Figure 9

TTA	Activity Coeff. TTA	Log TTA	E$\frac{b}{a}$	Log E
.01	.996	-2.001	.449	- .347
.01	.996	-2.001	.577	- .238
.02	.988	-1.704	2.34	.370
.02	.988	-1.704	2.59	.414
.04	.974	-1.409	14.49	1.162
.08	.943	-1.122	84.8	1.929

These data add strength to the conviction that the TTA power dependence at low acid is only 2 while at higher acids it approaches 4 as a limiting value. If this is true then at low acidities the reaction should be written as:

$$Hf(OH)^{+3} + 2\ HK \longrightarrow HfOK_2 + 3\ H^+$$

It seems probable that the TTA dependence curves of between 3 and 4 obtained in strong nitric acid are explainable by a mixture of the reaction above and the following:

$$Hf^{+4} + 4\ HK \longrightarrow HfK_4 + 4\ H^+ \quad (\text{or } 3\ H^+, \text{ if } Hf(OH)^{+3})$$
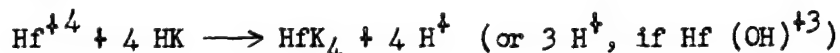
STUDIES WITH COMPLEXING IONS

(a) Bisulfate

Bisulfate complexing in the hafnium system was investigated by mixing $2\underline{M}\ H_2SO_4$ and $2\underline{M}\ HClO_4$ and extracting in the manner already described. The experiments were carried out at a constant TTA concentration of $0.1\underline{M}$ and in $2\underline{M}$ acid. The data are given in Table VIII.

TABLE VIII

Bisulfate Complexing in $2\underline{M}$ Acid and $0.1\underline{M}$ TTA Solutions

HSO_4^-	$Log\ HSO_4^-$	E_a^b	$Log\ E$	E_o/E	$E_o/E-1/HSO_4^-$
0.00	--	118.2	2.072	--	--
.033	-1.483	50.72	1.706	2.33	40.3
.064	-1.19	8.56	.933	13.8	200.0
.125	- .902	10.75	1.032	10.99	79.92
.286	- .543	2.82	.451	41.9	143.0
.67	-1.73	1.006	.000	117.4	173.0
1.00	.000	.731	- .135	161.0	160.0
1.34	.128	.607	- .216	194.0	144.0
2.00	.320	.344	- .463	343.0	171.0

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The data are evaluated from the following equation:

$$\frac{E_O}{E} = 1 + K_1(HSO_4^-) + K_2(HSO_4^-)^2 + K_3(HSO_4^-)^3 - - - - -$$

where E_O is the distribution ratio in the absence of any bisulfate, and E is the distribution ratio in the presence of various amounts of bisulfate.

By plotting E_O/E vs (HSO_4^-) (Figure 10) a line with slope K_1 is obtained. If higher complexes than that with one (HSO_4^-) per Hf are present, the curve gives a second slope, the value of which may be determined by the plot of $E_O/E - 1/(HSO_4^-)$ vs (HSO_4^-) (Figure 11).

Since the previous equation may be rearranged:

1. $E_O/E = 1 + K_1(HSO_4^-) + K_2(HSO_4^-)^2 - - - - -$
2. $E_O/E - 1/(HSO_4^-) = K_1 + K_2(HSO_4^-)$

The intercept then is K_1 and the slope of the line is K_2.

Within the limit of accuracy of the data, K_1 is 159 and K_2 is 0 or less than 3. Plotting log E vs log (HSO_4^-) (Figure 12) a slope of 1.05 is found. This indicates an average of one HSO_4^- per hafnium.

K_1 for the zirconium bisulfate complex has been reported (AECD-2272) as 231 and K_2 as 52.8.

(b) Nitrate

The effect of nitrate complexing on the extraction of hafnium was investigated in $HClO_4$ solution by adding NO_3^- in the form of $NaNO_3$. These data are summarized in Table IX.

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TABLE IX

Effect of Nitrate on Extraction

$2\underline{M}$ $HClO_4$ - solid $NaNO_3$, $.04\underline{M}$ TTA

$NO_3\underline{M}$	$E\frac{b}{a}$	E_o/E
0	6	--
.5	4.5	1.33
1.0	3.75	1.59
1.5	3.9	1.54
($2\underline{N}$ HNO_3) 2.0	2.69	2.23

These data then gave $K_1 = 0.61$ from

$$E_o/E = 1 + K_1(NO_3^-) \qquad \text{(Figure 13)}$$

This complexing correction was then applied to some of the data for comparison with that of Huffman and Beaufait (UCRL-194), and the results are given in Table X.

TABLE X

Equilibrium Constants Corrected for Nitrate Complexing

$E_o/E = 1 + K_1(NO_3)$ 　　　　　　　　 $E_o = E + EK_1(NO_3)$

$1.96\underline{N}$ H^+ 　　　　　　　$(NO_3^-) = 1.96$ 　　 $K_1 = .61$

TTA	$E\frac{b}{a}$	E_o	$K' \times 10^6$
.06	11.07	24.31	2.22
.02	.222	.488	3.19
.08	15.45	33.93	1.04
.04	2.70	5.93	2.56
.03	1.092	2.40	3.16
.10	59.8	131.32	1.75
			Av. 2.32×10^6

TABLE X

$$K' = \frac{E_o}{(TTA)^4}$$

$$\log K' = \log E^o - 4 \ (\log TTA)$$

3.32$\underline{N}$ H$^+$

$$K_1(NO_3) = .61 \times 3.32 = 2.025$$

TTA	$E_{\frac{b}{a}}$	E_o	$K' \times 10^6$
.06	2.16	6.53	.197
.10	13.84	41.87	.184
.04	.523	1.58	.226
.08	5.78	17.48	.178

Av. $.196 \times 10^6$

The average value of K' for 1.96$\underline{M}$ H$^+$ then we find to be 2.32×10^6. This is compared with 4.17×10^6 from Huffman and Beaufait data (or 3×10^6 if the average of only their tracer data is used).

Application of this method of calculation to the data at 3.32$\underline{M}$ H$^+$ gives a constant which is a factor of 10 lower when calculated in the same manner.

With the HClO$_4$ data at 2$\underline{M}$ H$^+$ we have:

TABLE XI

TTA	$E_{\frac{b}{a}}$	Log K'	K'
.02	.450	6.470	2.95×10^6
.04	6.00	6.515	3.27×10^6
.10	118.2	6.196	1.57×10^6

where K' is defined as before.

One concludes then that the nitrate complexing is quite small but, if accurately corrected for, the data agrees with work performed in non-complexing media.

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(c) Chloride

A few experiments were made in NaCl-HCl solution at an ionic
strength of 2 to see how markedly the system differed from the nitrate
system.

The data are collected in Table XII.

TABLE XII

Extraction of Hafnium from Chloride Solution

TTA	H^+	$E\frac{b}{a}$	Log E	Log H^+
.02	.6614	3.45	.538	- .180
.02	.8304	1.91	.281	- .081
.02	.5446	5.56	.745	- .264

These data when plotted in the form log E vs log H^+ (Figure 14)
give an acid power dependence of 3 as for HNO_3 solution. There is some
complexing as indicated by the lowering of the E values as compared
with those observed in nitrate solutions (Tables VI and VII), although
the data are not strictly comparable. In general it would appear that
chloride complexing is not strong, however.

(d) Other Ions

Qualitative tests were made to determine the order of magnitude
of the complexing that might be expected from oxalate and phosphate ions.

An aqueous phase that was $0.123\underline{M}$ in oxalic acid and $2\underline{M}$ in nitric acid,
and containing hafnium tracer was extracted with $0.1\underline{M}$ TTA in benzene for
two hours. The value of E thus found on equilibration was approximately
10^{-4}. In HNO_3 solution under the same conditions, the value of E is about
60.

For comparison, a zirconium tracer (freshly prepared by TTA extraction) solution was complexed with oxalate and equilibrated under identical conditions; no measurable extraction was found.

When the hafnium tracer was present in $.127\underline{M}$ H_3PO_4 and $2\underline{N}$ HNO_3 precipitation occurred. Further runs with phosphate were not attempted.

From these preliminary investigations it was concluded that no particular advantage could be gained by using complexes in the hafnium-zirconium separation by TTA. Each ion tested seemed to affect both elements in a similar manner and no advantage was apparent. For further data on complexing agents with zirconium see Connick and McVey, UCRL-101 (AECD-2272).

(e) Extraction Rates

(1) Hafnium

It has been known for some time, particularly from the work at the Oak Ridge National Laboratory, that the extraction rate for hafnium is much lower than for zirconium. Two series of experiments were undertaken to determine the rate in the nitric acid systems being used. Solutions having the indicated compositions (Tables XIII, XIV) were stirred for a given time, duplicate samples taken from each phase, then the stirring continued for another period. The process continued until no further change in E was observed.

The data are given in Table XIII for rates determined with two differing TTA solutions, at three acidities. The data are plotted in Figures 15 and 16.

TABLE XIII

Rate of Extraction of Hafnium

(.05M TTA)

1.95M HNO$_3$		1.55M HNO$_3$		1.06M HNO$_3$	
Min.	E	Min.	E	Min.	E
5	.295	5	.337	5	.347
10	.680	10	.752	10	.854
20	1.48	20	1.64	20	1.93
40	3.32	40	4.38	40	6.5
120	4.72	60	7.14	60	11.87
		90	9.29	60	12.8
		120	9.07	90	14.9
		180	9.11	120	13.9
				120	14.8

(.02M TTA)

1.95M HNO$_3$		1.466M HNO$_3$		1.06M HNO$_3$	
Min.	E	Min.	E	Min.	E
5	.035	5	.065	5	.106
15	.124	15	.268	15	.265
30	.204	30	.489	30	.494
120	.224			120	2.08

These data show that it takes 80-90 minutes to reach equilibrium under
the conditions used. Zirconium, as shown subsequently, is extracted to its
equilibrium value under various conditions in considerably less time.
Therefore, by contacting for periods less than 10 min. the E value for
hafnium may be kept under one while zirconium has an E value over one.

PART II ZIRCONIUM

RATE STUDIES

An attempt was made to study the rate of extraction of zirconium by TTA, using macro amounts of zirconium. Although results were not entirely reproducible, general trends could be established.

Experimental Method

Aqueous solutions .00015 - .00085$\underline{M}$ were made by diluting a zirconium solution in 5.8$\underline{N}$ HNO$_3$ with solutions 2 molar in NO$_3^-$ to obtain the desired acidity. Ionic strength was kept very near 2 in all cases. These were contacted with an equal volume of the TTA solution in a small closed extractor described previously. The extractor was immersed in a water bath at $25^{\circ} \pm 0.5^{\circ}$. At intervals stirring was stopped, the phases allowed to settle 1 minute, and equal volumes withdrawn from each phase. Zirconium in the aqueous phase was determined colorimetrically using the alizarin method of Liebhafsky and Winslow, J. Am. Chem. Soc. $\underline{60}$, 1776 (1938). The concentration in the organic layer was calculated by difference.

A. Dependence of Zirconium Concentration

It was found that the rate of extraction shows a first power dependence on the zirconium concentration which is to be expected. See Figure 17.

B. Acid Dependence

The rate of extraction apparently depends on the acid concentration, but the data did not prove good enough to permit an analysis.

The experimental curves are given in Figure 18. With a hydrogen ion concentration less than 0.6, the zirconium is extracted more slowly, which may indicate a different species extracted or colloid formation. No further work was done in this range of acidity. The experimental conditions used were: .02 molar TTA, 0.6N - 2.15N H+, with a total NO_3^- concentration of 2.1M, and 0.00034M zirconium. The low concentration of zirconium was used to keep the TTA concentration nearly constant throughout the experiment.

C. TTA Dependence

In a similar fashion the rate of attainment of equilibrium was dependent upon the TTA concentration. Experimental conditions were: 2.04N HNO3, 0.01 - 0.05M TTA and 0.00015M zirconium. Results are shown in Figure 19.

It should be noted that all rate measurements were made starting with the zirconium in the aqueous phase. The rate of re-extraction from benzene has not been measured over short time intervals, but apparently is much lower than corresponding to extraction from the aqueous phase under comparable conditions. This factor is of importance in any continuous process involving extraction and scrub steps (see Part III).

CHECK ON EQUILIBRIUM EXPRESSION

The expression for the chelation of zirconium in acid is thought to be: (UCRL-126)

$$Zr(OH)^{+3} + 4 \ HK \ \rightleftharpoons \ ZrK_4 + 3 \ H^+ + H_2O$$

$$K = \frac{(Zr)_o \ (H^+)^3}{(Zr)_a \ (HK)^4} = 3 \times 10^8$$
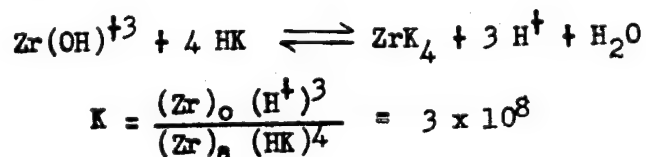
This value was checked at a few isolated points, and the results, given in Table XIV, lead to an average value of 1.3×10^8. Values are given in the table for K_c' corresponding to the reaction:

$$Zr^{+4} + 4\ HK \rightleftharpoons ZrK_4 + 4\ H^+$$

$$K_c' = \frac{(Zr)_o\ (H)^4}{(Zr)_a\ (HK)^4}$$

but from these incomplete data it cannot be determined which expression is better.

TABLE XIV

Zirconium Chelation with TTA at Equilibrium

$(Zr)_a$ γ/ml orig.	$(Zr)_a$ γ/ml at t.	t min.	$(H^+)_a$	$(TTA)_o$	E_c	$K_c \times 10^{-8}$	$K_c' \times 10^{-8}$
96.3	31.5	20	1.98	.02	2.03	.985	1.96
57.4	14.6	30	2.	.02	2.93	1.46	2.92
79.1	21.6	30	2.	.02	2.66	1.33	2.66
64.1	20.4	60	1.95	.02	2.13	.986	1.92
[64.1	30.5	30	1.99	.02	1.11	.546	1.09]
55.1	15.8	40	2.	.02	2.49	1.25	2.50
55.1	16.2	55	2.	.02	2.39	1.19	2.38
[55.1	<0.5	45	1.42	.02	~100.	17.9	25.4]
55.1	43.4	45	2.04	.012	0.27	1.11	2.26
55.1	12.5	45	1.02	.012	3.41	1.75	1.78

$$K_c = \frac{(Zr)_o\ (H^+)^3}{(Zr)_a\ (TTA)^4}$$

$$K_c' = \frac{(Zr)_o\ (H^+)^4}{(Zr)_a\ (TTA)^4}$$

(Av. of 9) $1.18 \pm .23$ $2.16 \pm .46$

(Av. of 8) $1.26 \pm .19$ $2.30 \pm .30$

EFFECT OF TEMPERATURE UPON THE EXTRACTION OF ZIRCONIUM

A few runs were made at higher temperatures (see Table XV) to determine the extent to which zirconium would be extracted under conditions markedly

different from room temperature. Radio-zirconium was used for these experiments--the stock solution being prepared by extraction into TTA. In one case the TTA solution was back-extracted with $10\underline{N}$ HNO$_3$, which was used immediately as the stock solution; in the others, the $0.1\underline{M}$ TTA solution was diluted and used for the equilibration.

TABLE XV

Effect of Temperature on the Extraction of Zirconium with TTA

Temp. °C	Time min.	(TTA)	(H$^+$)	Counts aq.	Counts bz	E
40°	10	.02*	1.98	1800	5082	2.82
	20			2246	4707	2.10
	30			2345	4216	1.80
50°	10	.02*	1.98	2707	4232	1.56
	20			3190	3355	1.05
	30			3410	3365	0.99
50°	10	.02	1.93*	1844	1136	0.62
	20			1330	2370	1.78
	30			1131	2063	1.82
	40			1241	2180	1.76

* Phase in which zirconium was placed originally.

It is seen that under comparable conditions of acidity and TTA concentration, the distribution ratio for zirconium is lower at 50°C (E = 0.99) than at room temperature (E = 2.03, Table XIV, first experiment).

EFFECT OF TEMPERATURE ON THE DISTRIBUTION RATIO OF TTA

It was thought the difference in extraction coefficients of zirconium at higher temperature might be due to a decrease in the concentration of TTA in the benzene phase. This was not found to be the case, however. (See Table XVI). TTA concentrations were determined spectrophotometrically at 292 mμ, using an extinction coefficient K = 8 x 10^3. As nitrate has some absorption at this wavelength, blanks and dilutions of the benzene sample were made up to the same nitrate concentration.

TABLE XVI

Effect of Temperature on Distribution Ratio of TTA

Temp. C	Time hr.	(TTA) aq	(TTA) bz	Aq. Phase	E_c
25°	1	0.00237	0.092	$2\underline{N}$ HNO$_3$	38.8
40°	1	0.00159	0.0963	$2\underline{N}$ HNO$_3$	60.6
	2	0.00159	0.069		43
	2.5	0.00150	0.064		42.7
50°	1	0.00141	0.0969	$2\underline{N}$ HNO$_3$	68.7
40°	1	0.000602	0.0953	$2\underline{M}$ NaNO$_3$	158
	2	0.000727	0.103		142
	3	0.000781	0.0962		123

The value obtained at room temperature checks that reported previously
(UCRL-101, etc.). At 50°C the concentration of TTA in the acid aqueous
phase is about 60% as great as at room temperature, and this figure is
decreased by about half again in the presence of $2\underline{M}$ sodium nitrate.

PART III   SEPARATIONS

On the basis of data obtained, it appears that zirconium should be
separated from hafnium in nitric acid solution under both equilibrium and
non-equilibrium conditions. In the former case it becomes possible to
calculate, for an acid and TTA concentration, and using the appropriate
stoichiometry, the distribution ratios for each element separately.

The zirconium can always be extracted with a higher coefficient than
the hafnium, although the range of acid and TTA concentrations over which
E for hafnium is less than 1 (and E for zirconium is greater than 1) is not
large, as may be seen from inspection of the data in Tables I to VII.

It will be noted that in general the TTA concentration is of the order of 0.02 to 0.03 molar to obtain such E values, and in acid strong enough to exclude possible hydrolysis effects. Weaker acid leads to even higher distribution ratios, while increasing the acid concentration would permit use of higher concentrations of TTA. There may well be no advantage in this, however, as the solubility of the chelate in benzene represents a definite boundary condition. This solubility is probably no greater than $0.09\underline{M}$.

Extraction under non-equilibrium conditions is at this writing an empirical process. It has not been possible to make kinetics measurements of sufficient accuracy to define the order of the chelation reaction with respect to metal, hydrogen, and chelate ions although previous data have shown a definite rate dependence on each. The fact that the zirconium reaction is more rapid, under comparable conditions, than that for hafnium, as well as leading to a higher distribution ratio, lends attractiveness to the possibility of operating a separations process under non-equilibrium conditions at short contacting times. The success of such a process would depend, among other things, on the efficiency of the contacting in both extraction and scrub stages. This factor is one that makes significant kinetics data difficult to obtain, and would almost certainly make process control difficult.

To test the feasibility of separating hafnium and zirconium using a batch process, a solution containing both hafnium and zirconium in nitric acid was extracted, the organic phase scrubbed with acid, and this re-extracted. The flowsheet was as follows:

Feed:	10 ml 2M HNO$_3$ containing 0.281 mg Zr/ml + tracer Hf. Contact with 10 ml 0.05M TTA for 11 min.		
	Aqueous: 0.055 mg/ml Zr 20760 c/m/ml Hf	Benzene: 0.228 mg/ml Zr 6700 c/m/ml Hf Dilute 9.5 ml with 19 ml benzene Scrub with 10 ml 10M HNO$_3$ 30 min.	
		Benzene: 0.013 mg/ml Zr 80 c/m/ml Hf	Aqueous: 0.178 mg/ml Zr 6000 c/m/ml Hf Dilute 9 ml with 36 ml H$_2$O Contact with 20 ml 0.05M TTA for 10 min.
			Benzene: 0.172 mg/ml Zr 953 c/m/ml Hf
			Aqueous: 0.0034 mg/ml Zr 817 c/m/ml Hf

In all, four runs were made using this flowsheet, and in each the concentration of zirconium and the activity of the hafnium in the feed remained essentially unchanged. The data are contained in Table XVII.

TABLE XVII

Extraction of Mixture of Hafnium and Zirconium

Run	E, First Extraction		E, Scrub		E, Second Extraction	
	Hf	Zr	Hf	Zr	Hf	Zr
1	0.39	5.5	0.020	0.026	0.27	1.88
2	0.32	4.1	0.011	0.073	1.18	21.6
3	--	2.6	--	0.040	--	8.63
4	0.15	--	0.054	--	1.06	--

Although there are too few data to permit the drawing of broad conclusions, certain indications are clear. The first extraction may be made with an average zirconium recovery of about 80% under which conditions approximately 20% of the original hafnium is carried into the benzene phase with the zirconium. Higher zirconium recoveries are certainly desirable, and, as data in Part II indicate, may be attainable if higher TTA concentrations are used, although this may well be at the expense of a poorer separation, per stage, from hafnium. Additional work is a clearly indicated necessity for establishing the optimum operating conditions. At higher TTA concentrations it might be possible to make relatively short contact times, of the order of a few minutes, thus permitting the use of column or mixer-settler type equipment.

The data indicate the scrubbing operation with $10\underline{M}$ HNO_3 to be reasonably complete. The benzene raffinate will contain at most 1% of its original hafnium and zirconium, plus the TTA liberated when the chelates are decomposed by the acid. Purification of the benzene and recovery of the TTA are steps that require further study, but it should be possible to scrub the benzene with dilute alkali ($0.5\underline{M}$ or less; too strong alkali causes cleavage of the ketone) to extract the TTA and decompose the residual chelates. The aqueous extract, acidified with sulfuric acid (to hold back the hafnium and zirconium), could then be extracted with a small volume of benzene to obtain the free TTA as a concentrated benzene solution.

The data on the second extraction leave much to be desired; in Run #1 the zirconium loss is high, while in Run #2 a poor separation from hafnium is obtained. The ratio of the coefficients is about that expected, however,

which leads to the belief that factors other than chemical ones are involved. In Run #4, the benzene from the HNO_3 scrub was used directly for the second extraction, after adding TTA to bring the concentration up to 0.05$\underline{M}$.

SUMMARY

1. The extraction of hafnium by TTA has been studied in nitric acid as a function of acidity and TTA concentration.

2. The complexing of hafnium by nitrate and sulfate ions has been measured.

3. The rate of extraction of hafnium by TTA has been measured.

4. The previously reported values for the zirconium chelation constant have been checked under comparable conditions.

5. The rate of zirconium extraction as a function of acidity and TTA concentration has been measured.

6. The seperation of hafnium and zirconium in a mixture has been studied.
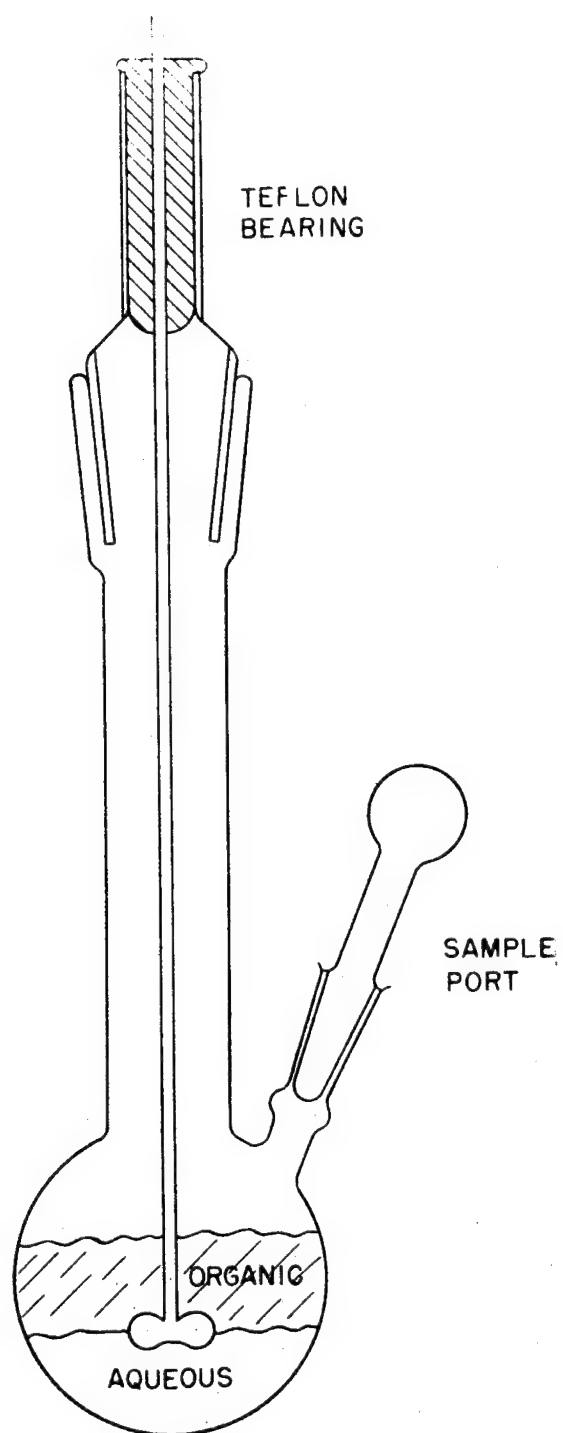
TEFLON
BEARING

SAMPLE
PORT

ORGANIC

AQUEOUS

EXTRACTION VESSEL

FIG. I

FIG. 2

FIG. 3

FIG. 4

T.T.A. POWER DEPENDENCE

CONSTANT ACID = 1.96 $\underline{N}$
CONSTANT IONIC STRENGTH = 2

S = 3.47

LOG E

LOG TTA $\underline{M}$

-30-

FIG. 5

FIG. 6

FIG. 7
-33-

FIG. 8

FIG. 9

FIG. 10

FIG. II

HSO₄⁻ COMPLEXING IN

HClO₄ SOLU. { 2 M ACID
0.1 M T.T.A.

S = 1.05

FIG. 12

NITRATE COMPLEXING OF Hf*

CONDITIONS $\begin{cases} 2\underline{M} \ HClO_4 + SOLID \ NaNO_3 \\ .04 \ \underline{M} \ T.T.A. \end{cases}$

$S = K_1 = 0.61$

$\frac{E_0}{E}$

$\underline{M} \ NO_3^-$
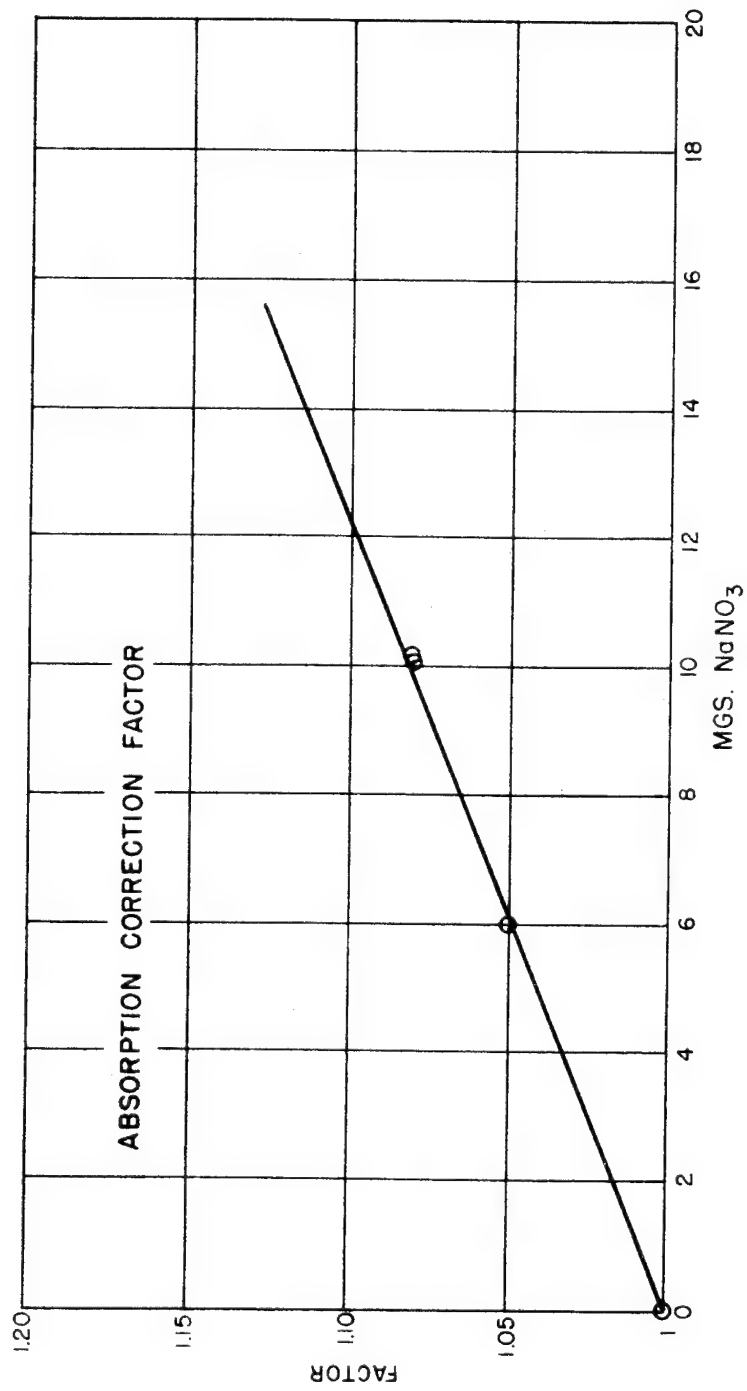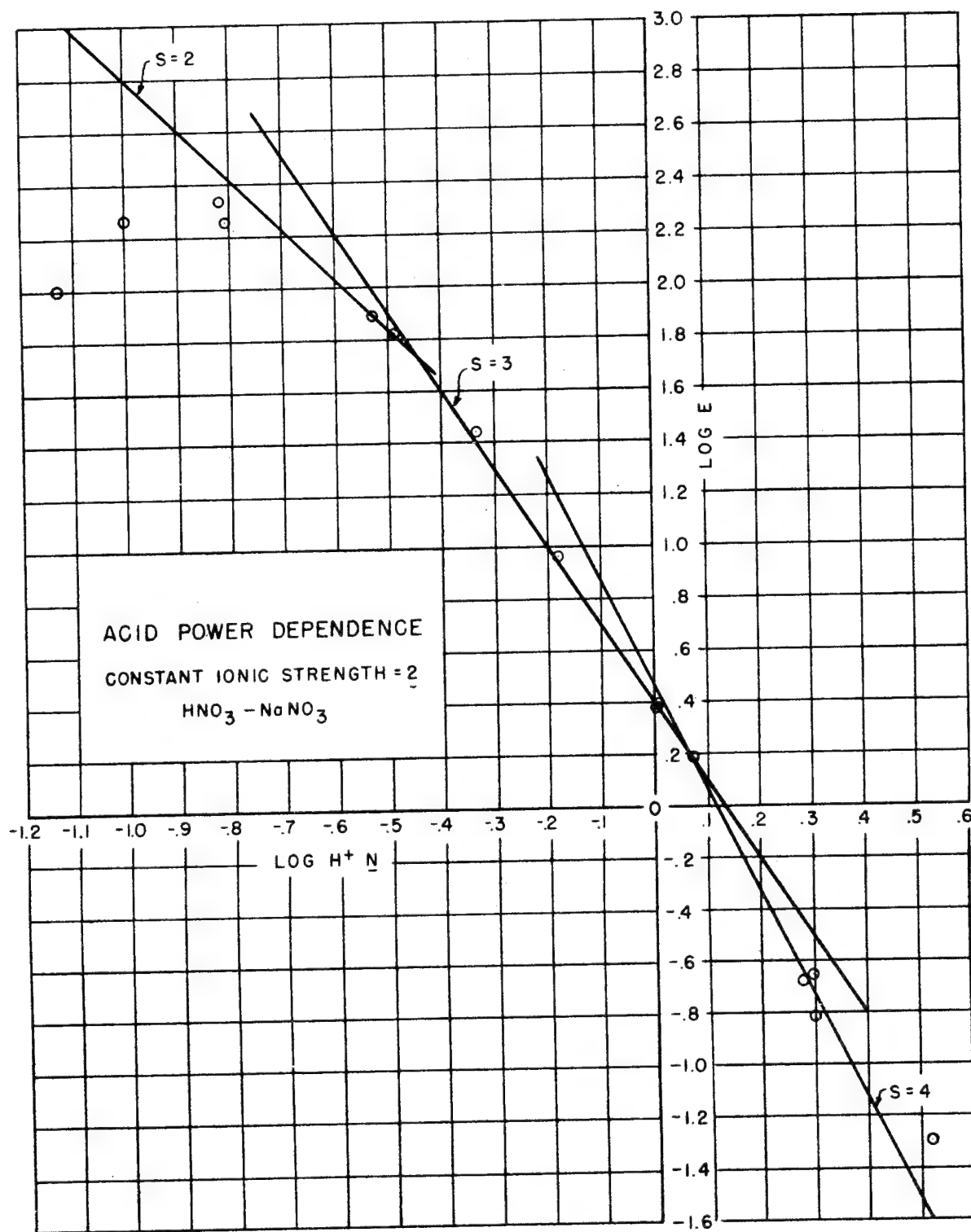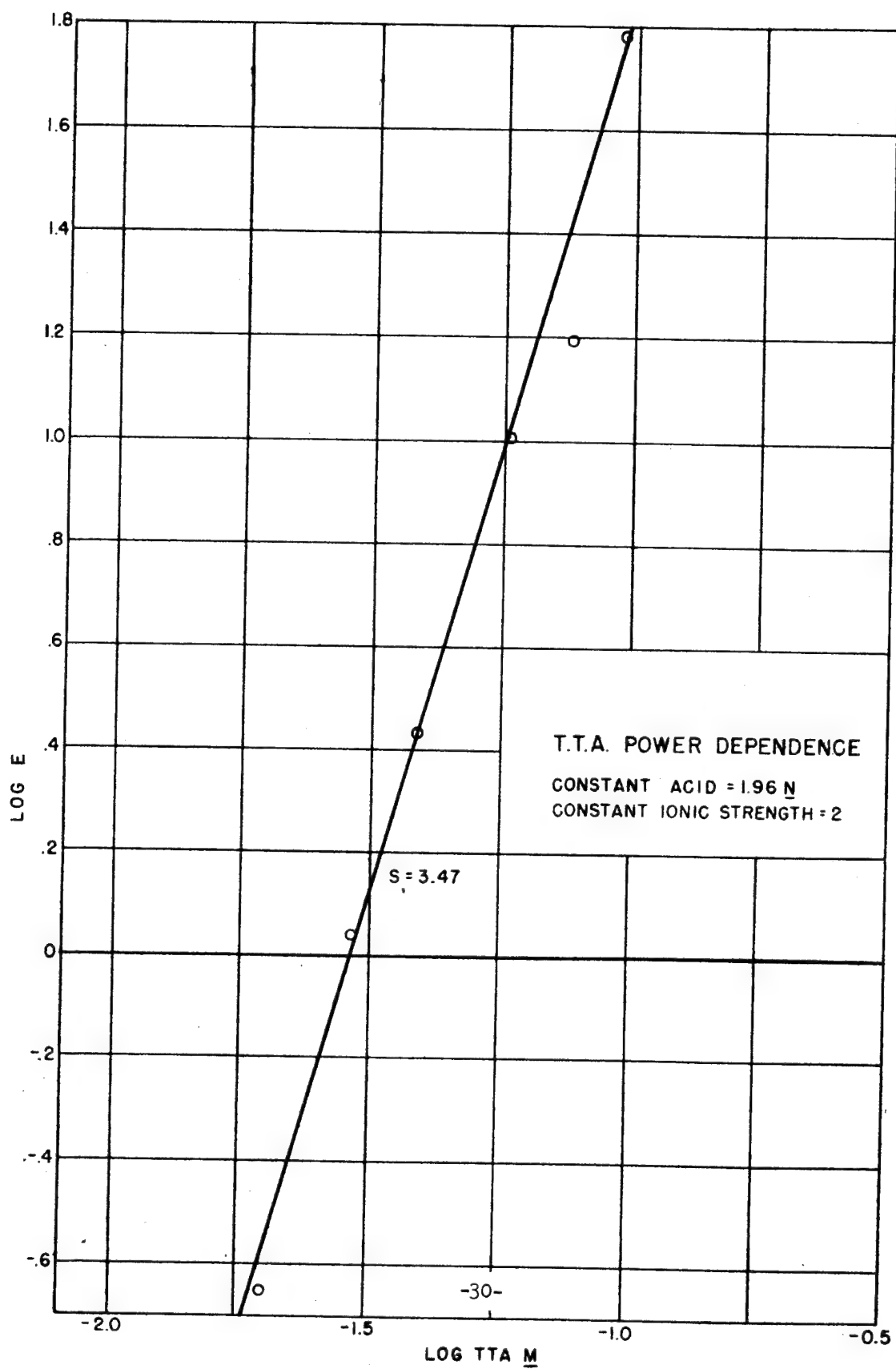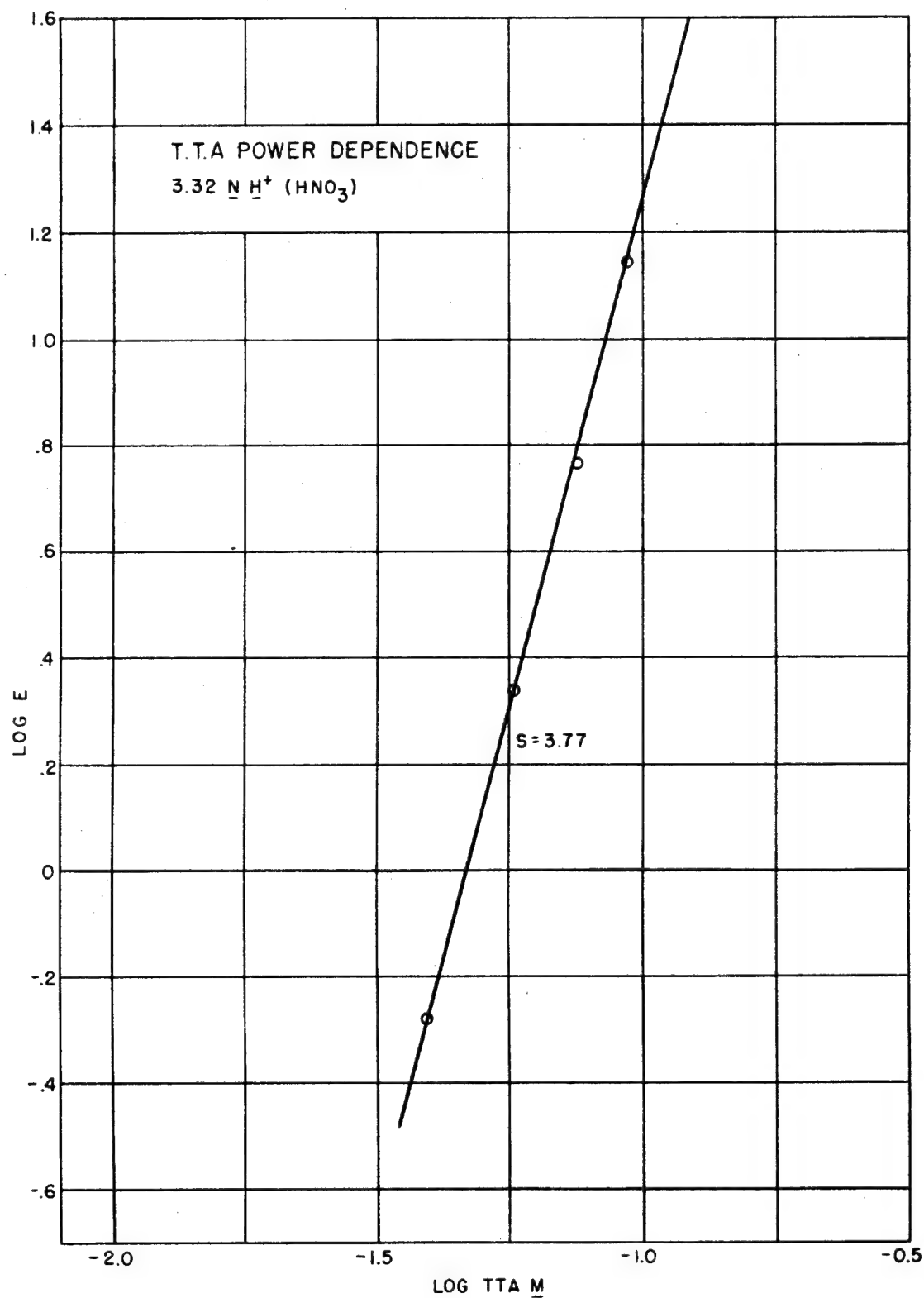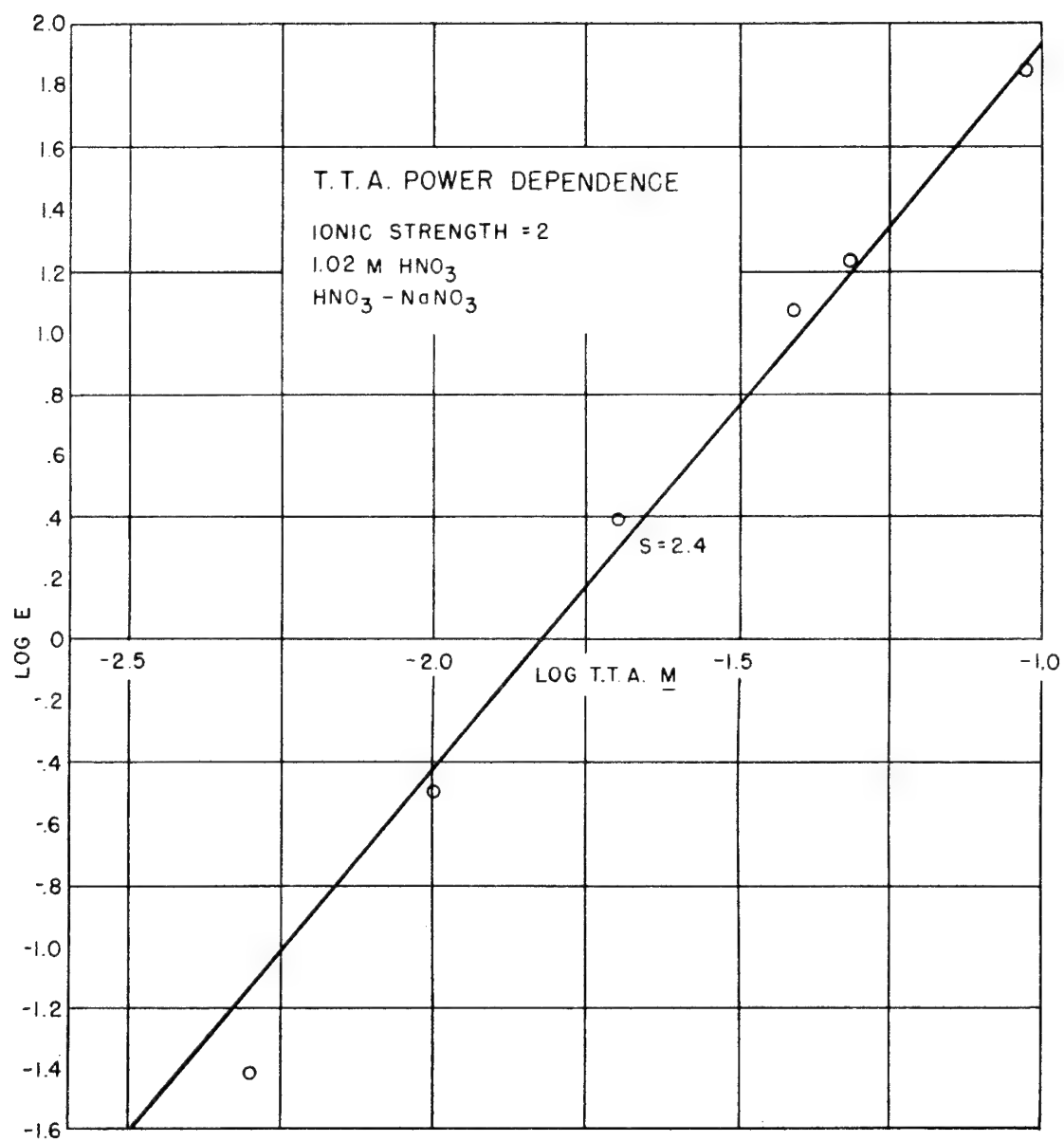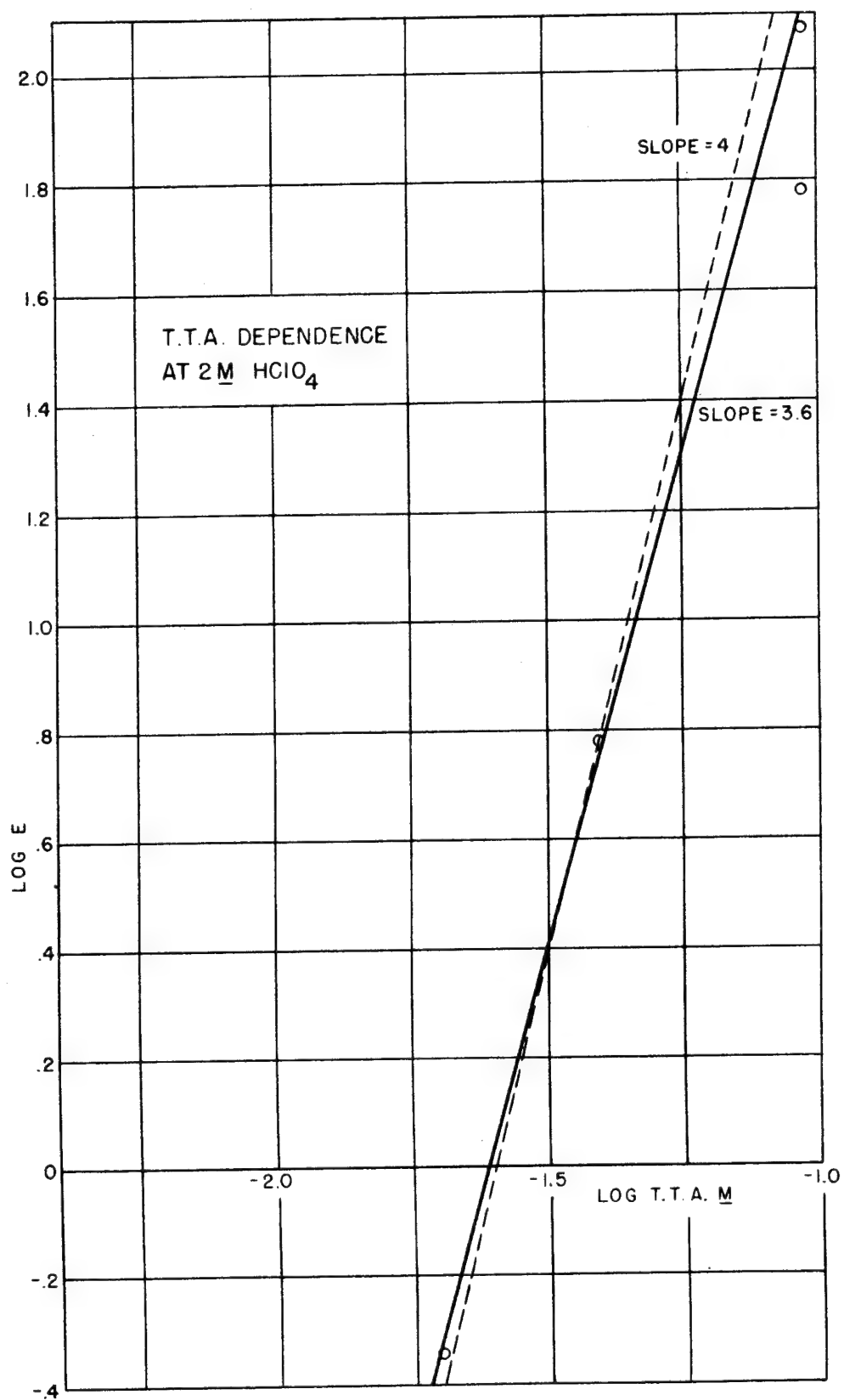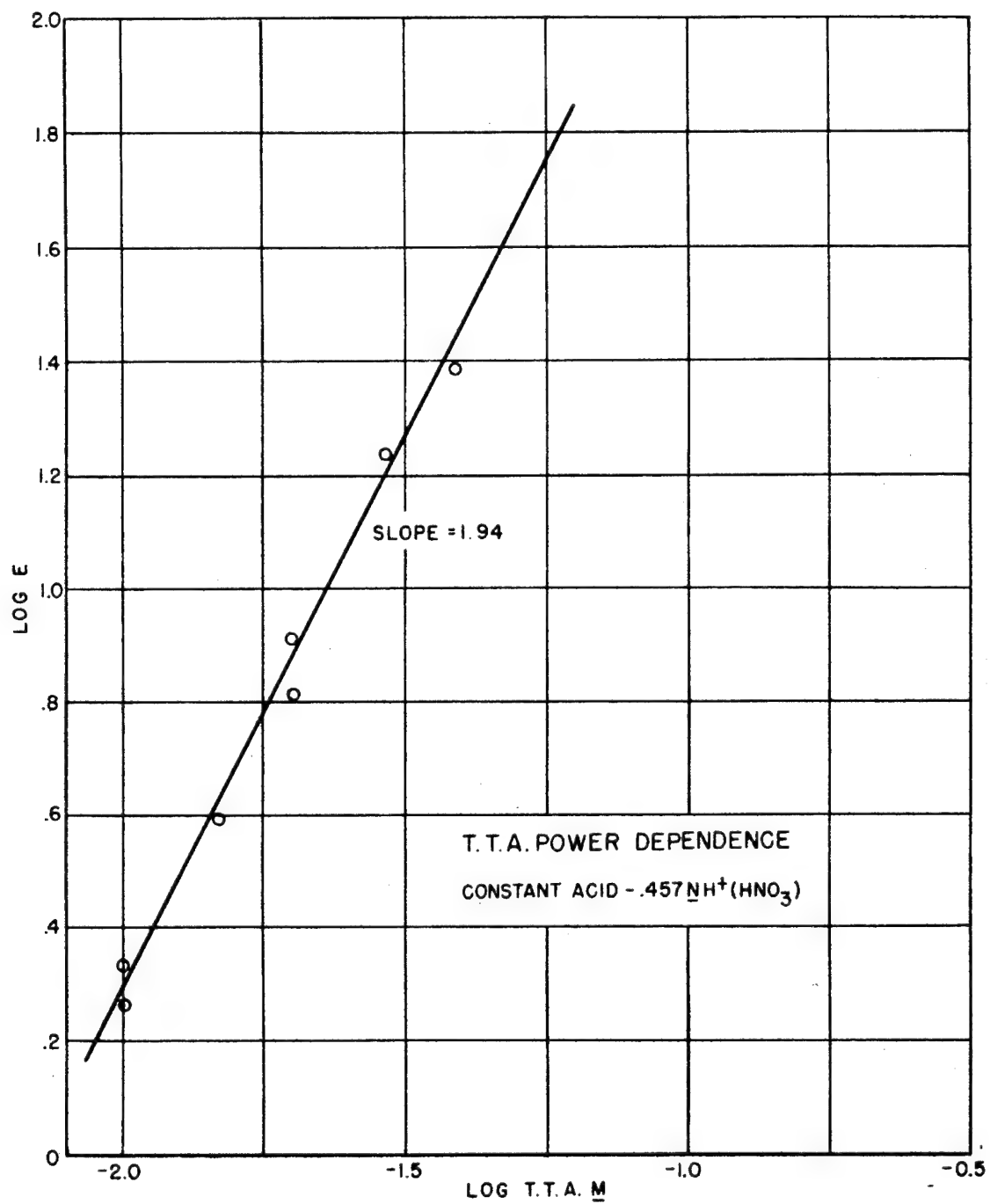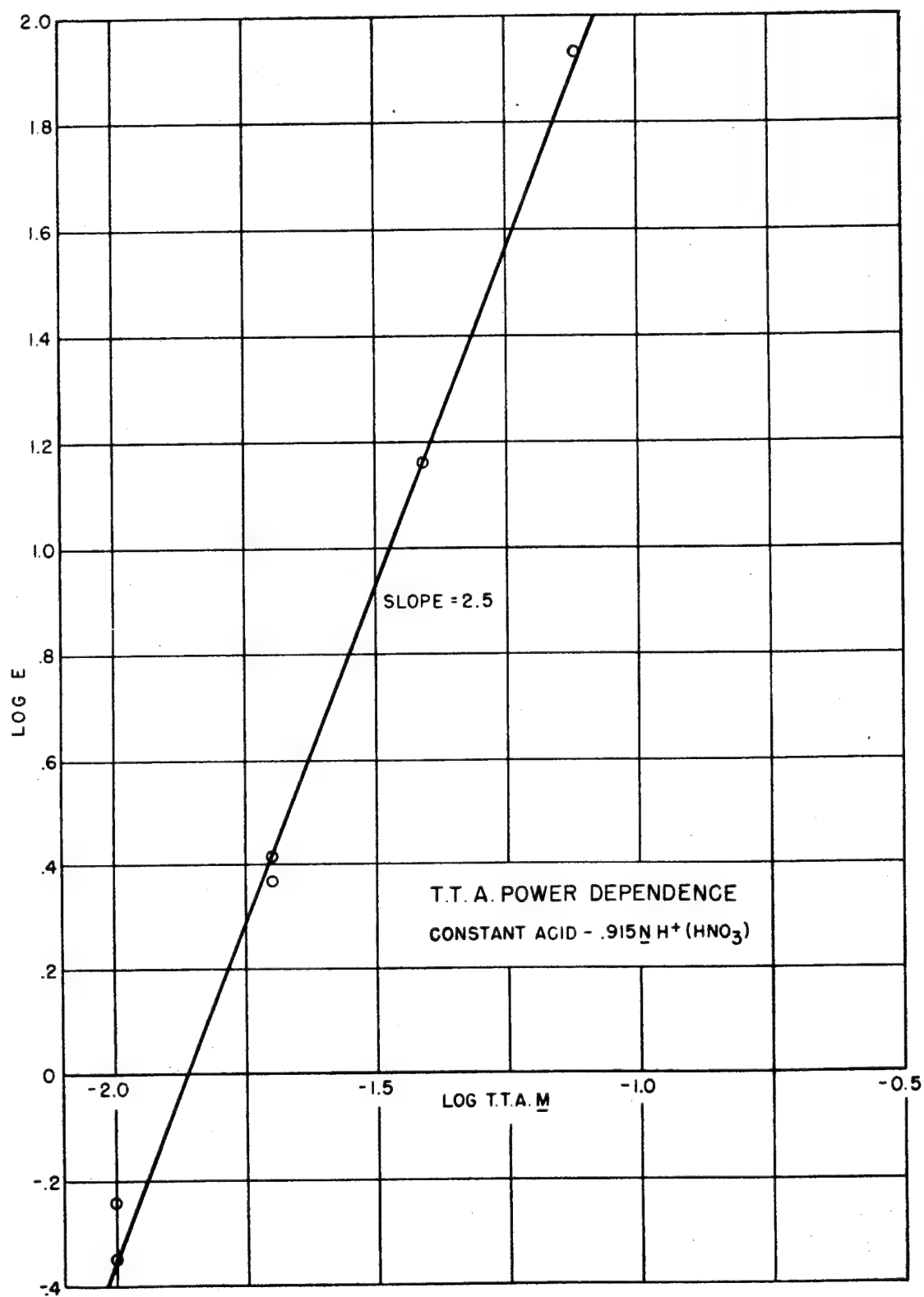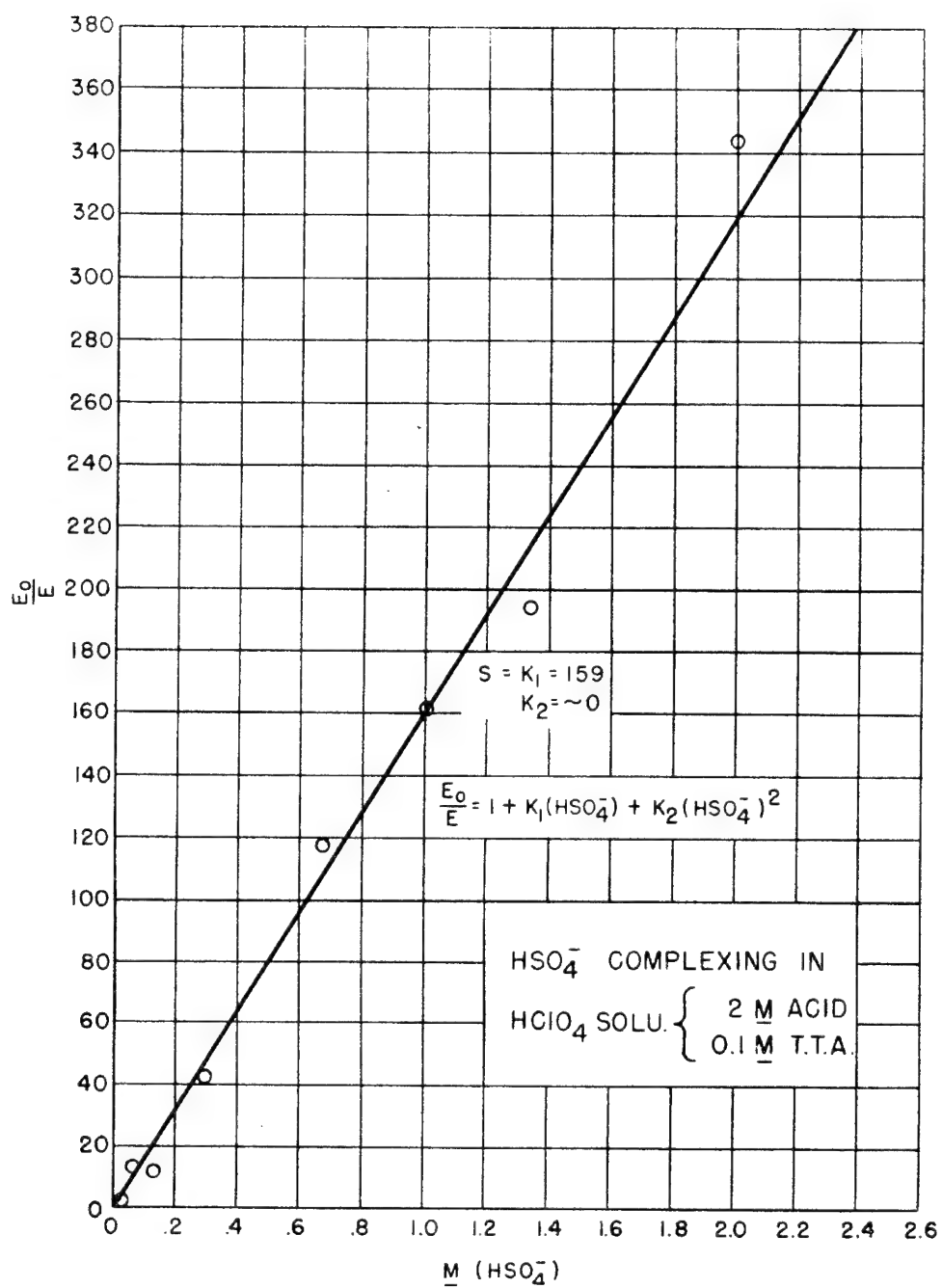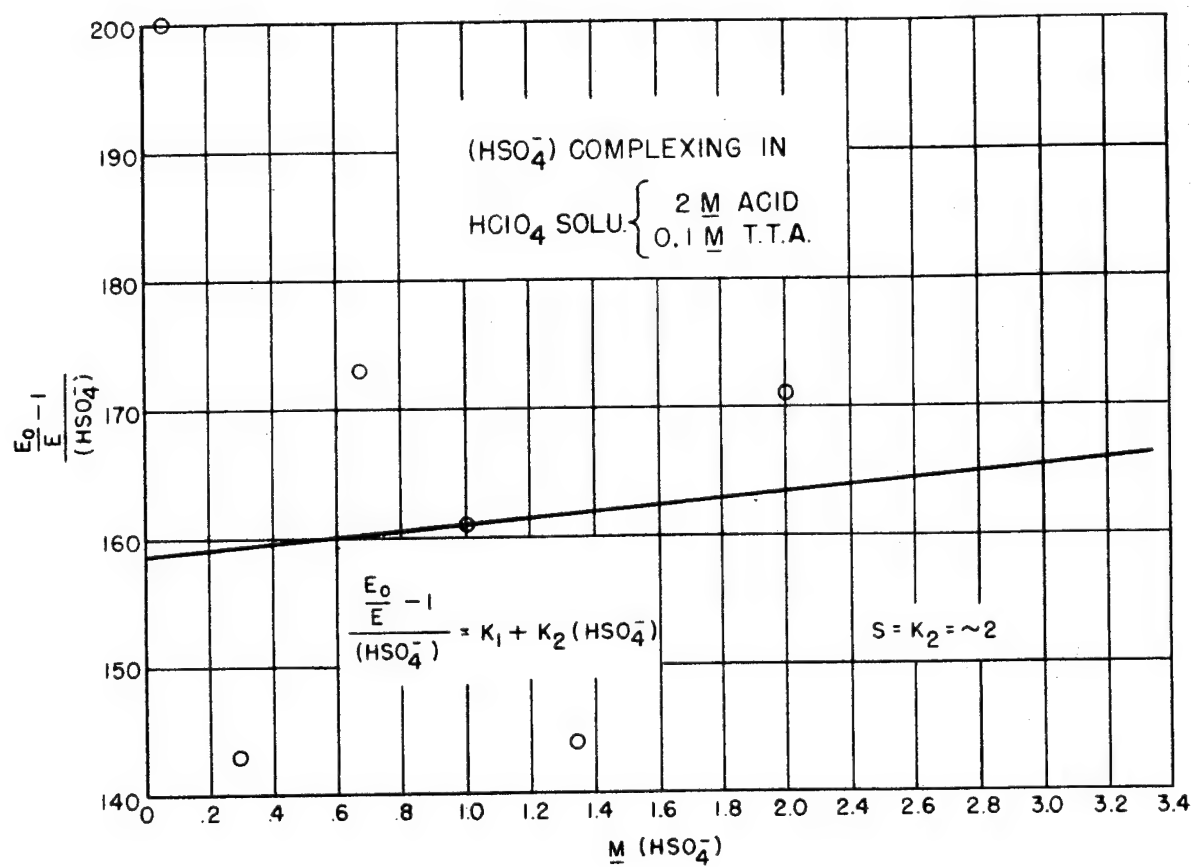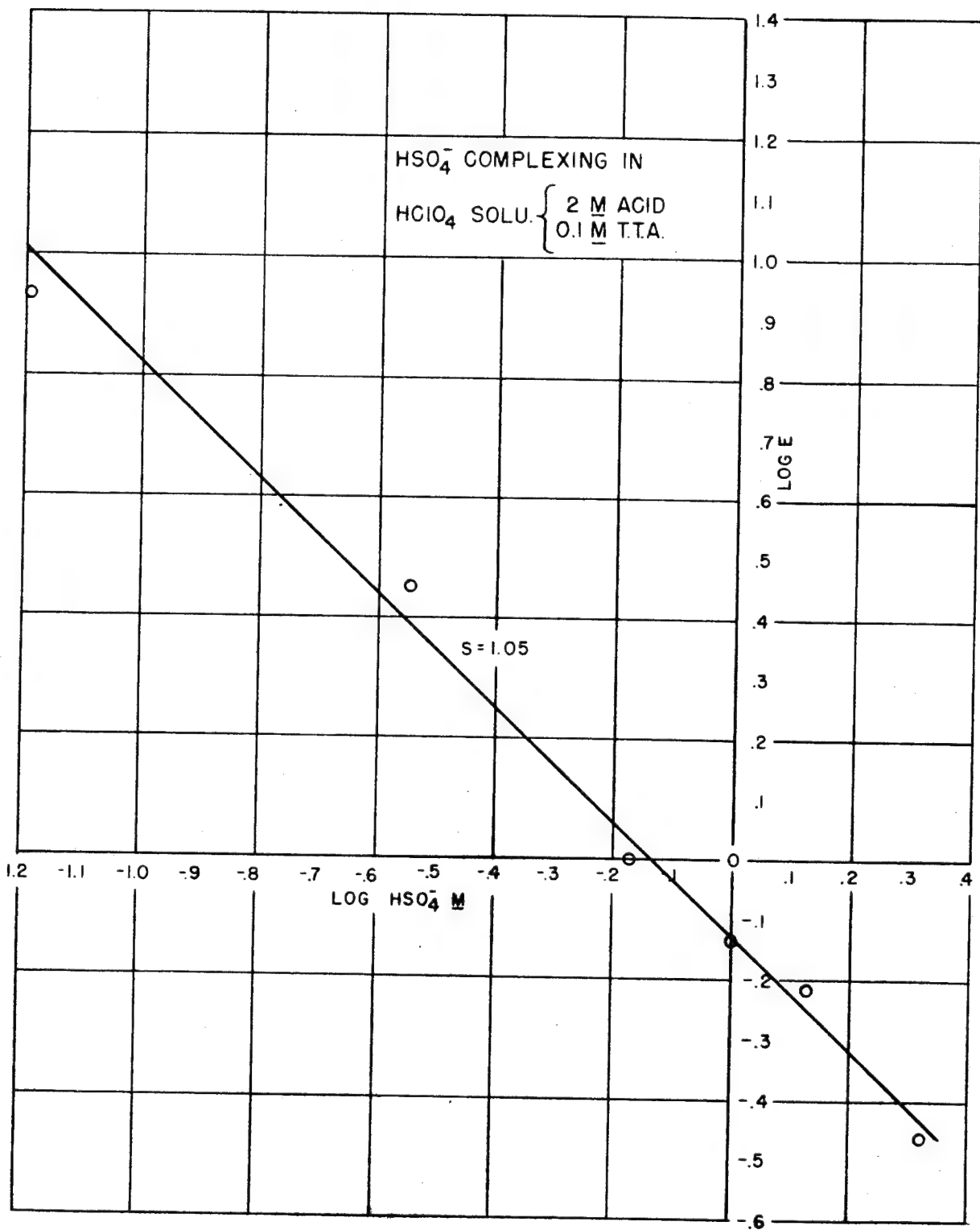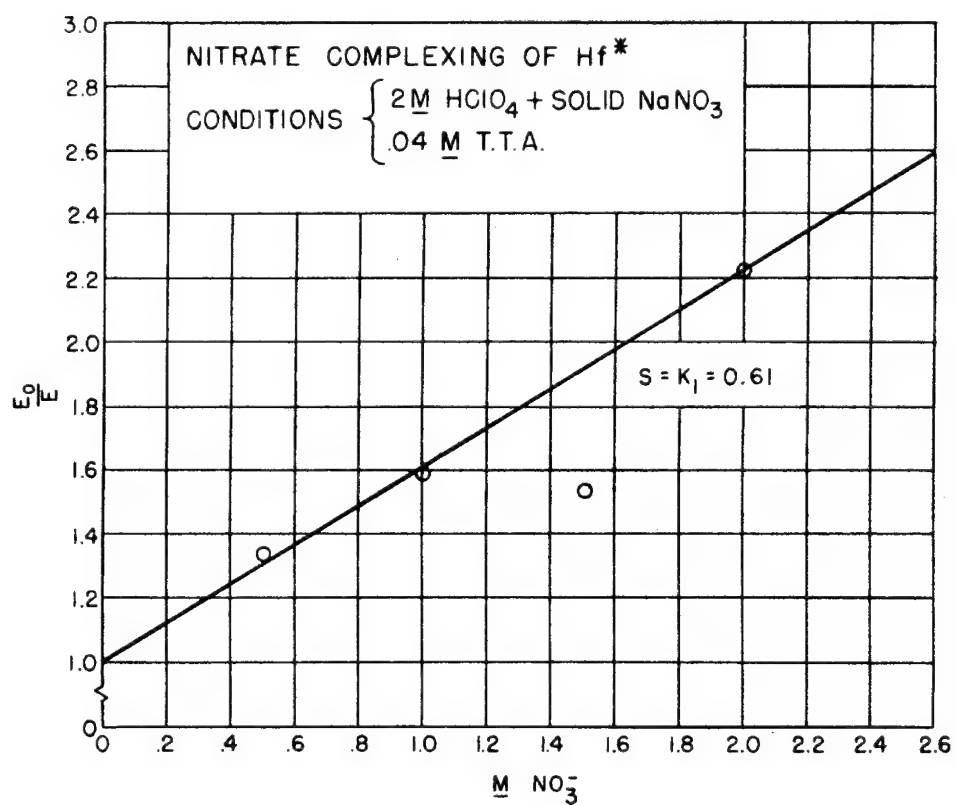
F.IG. 13
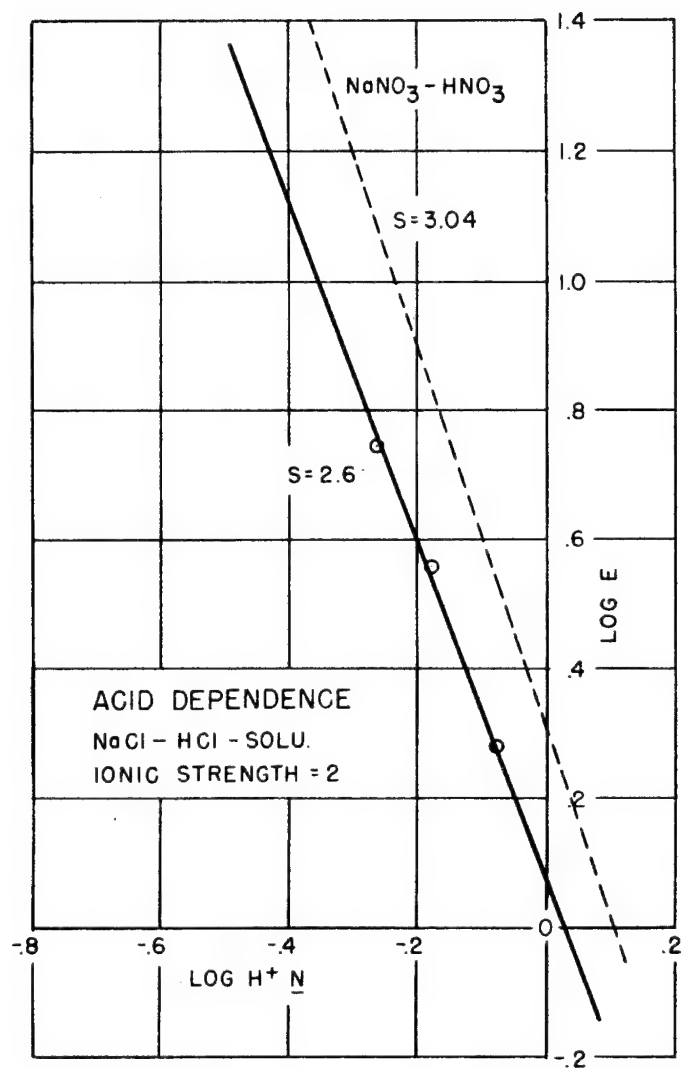
FIG. 14
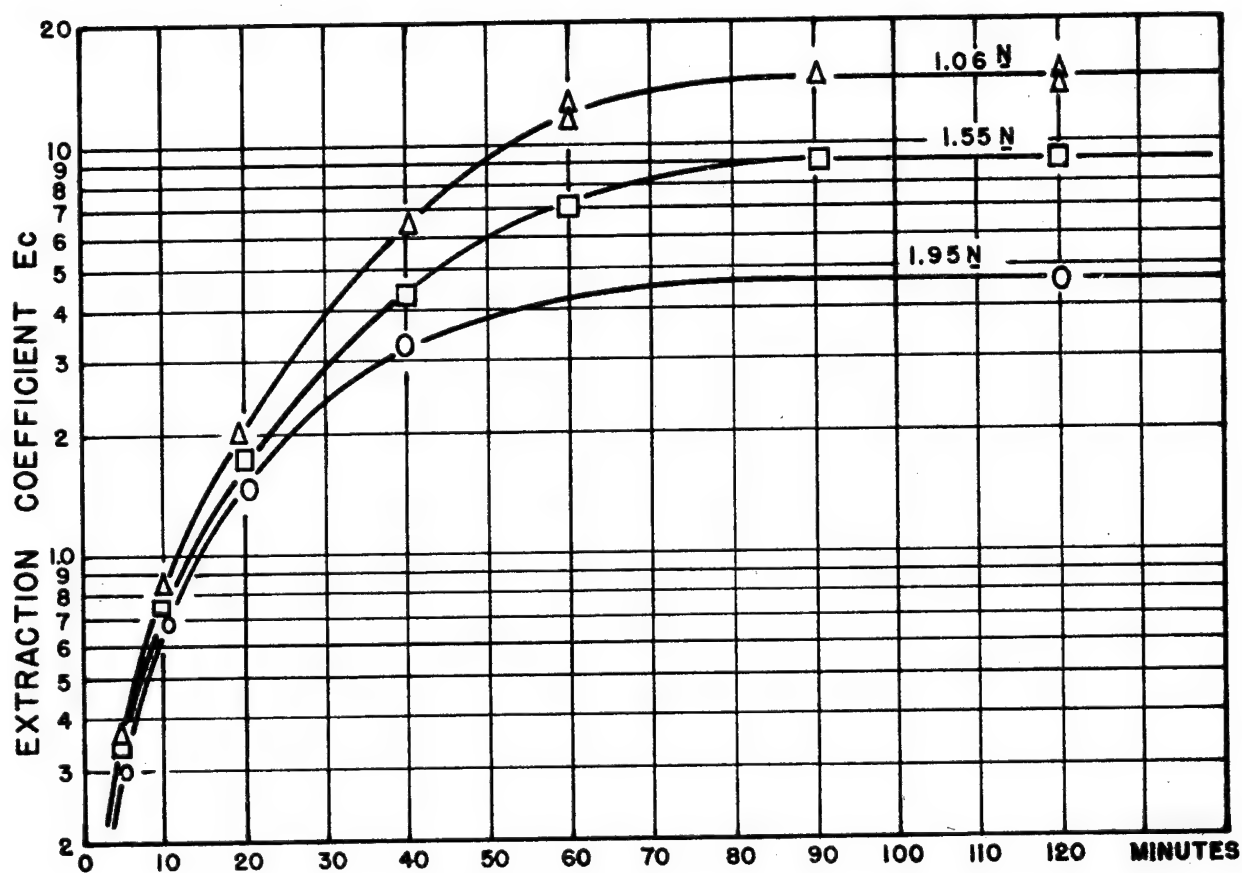
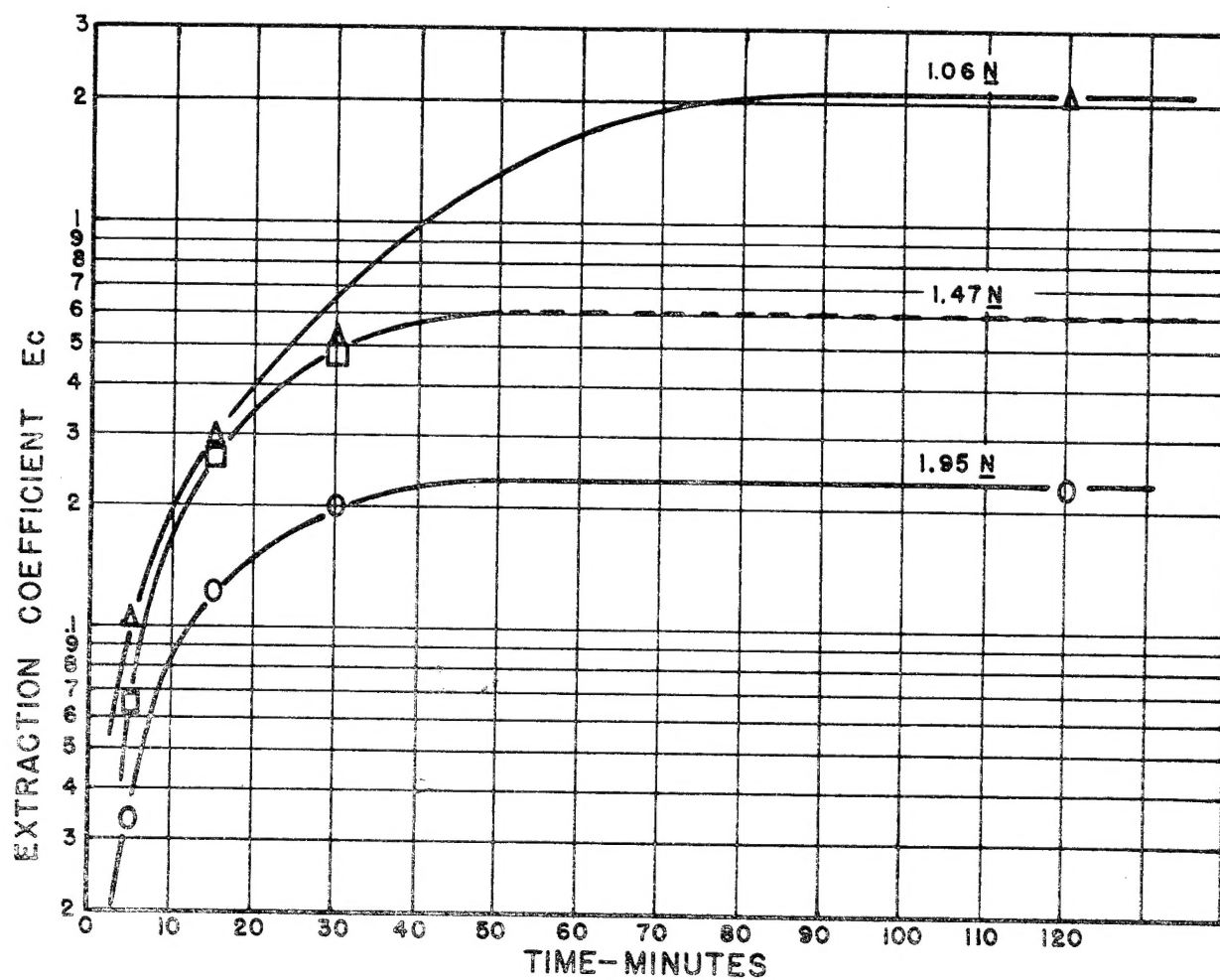FIGURE 15
HAFNIUM EXTRACTION FROM HNO₃
SOLUTIONS WITH .05 M TTA

FIGURE 16
HAFNIUM EXTRACTION FROM HNO_3
SOLUTIONS WITH .02 $\underline{M}$ TTA
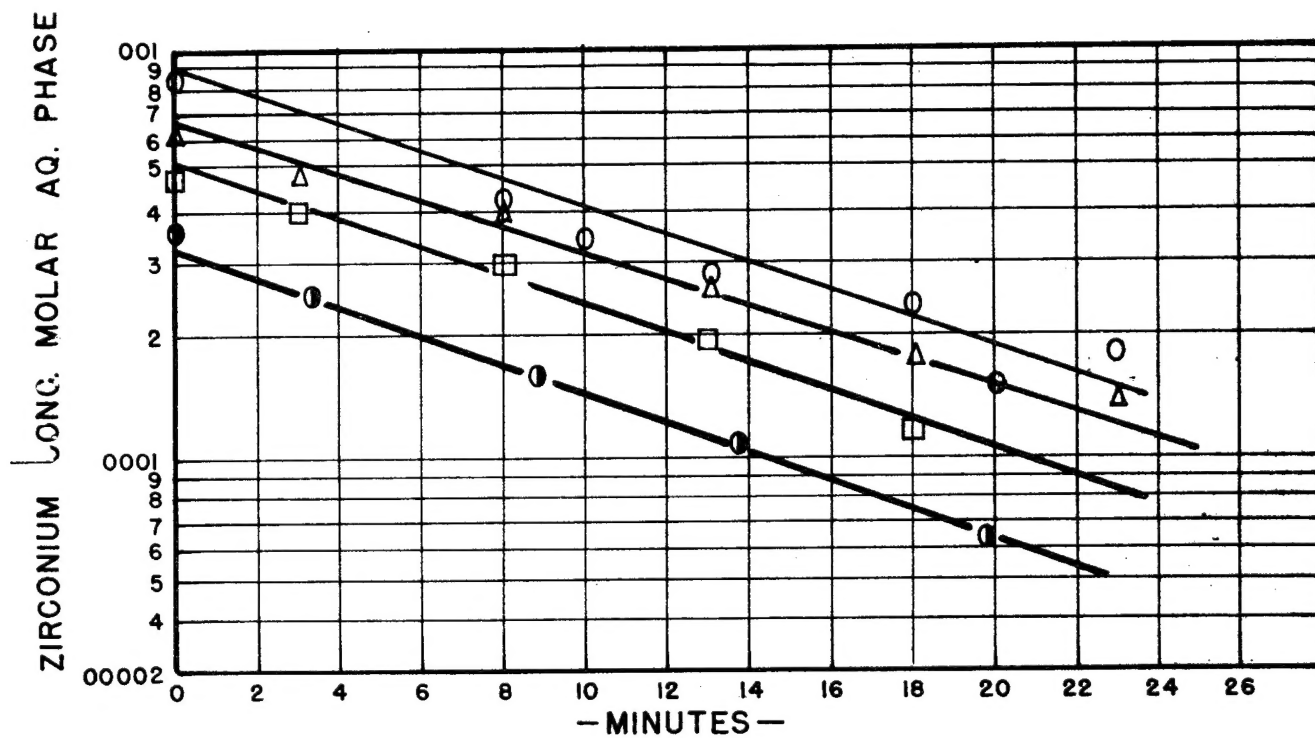
FIGURE 17

ZIRCONIUM EXTRACTION RATE

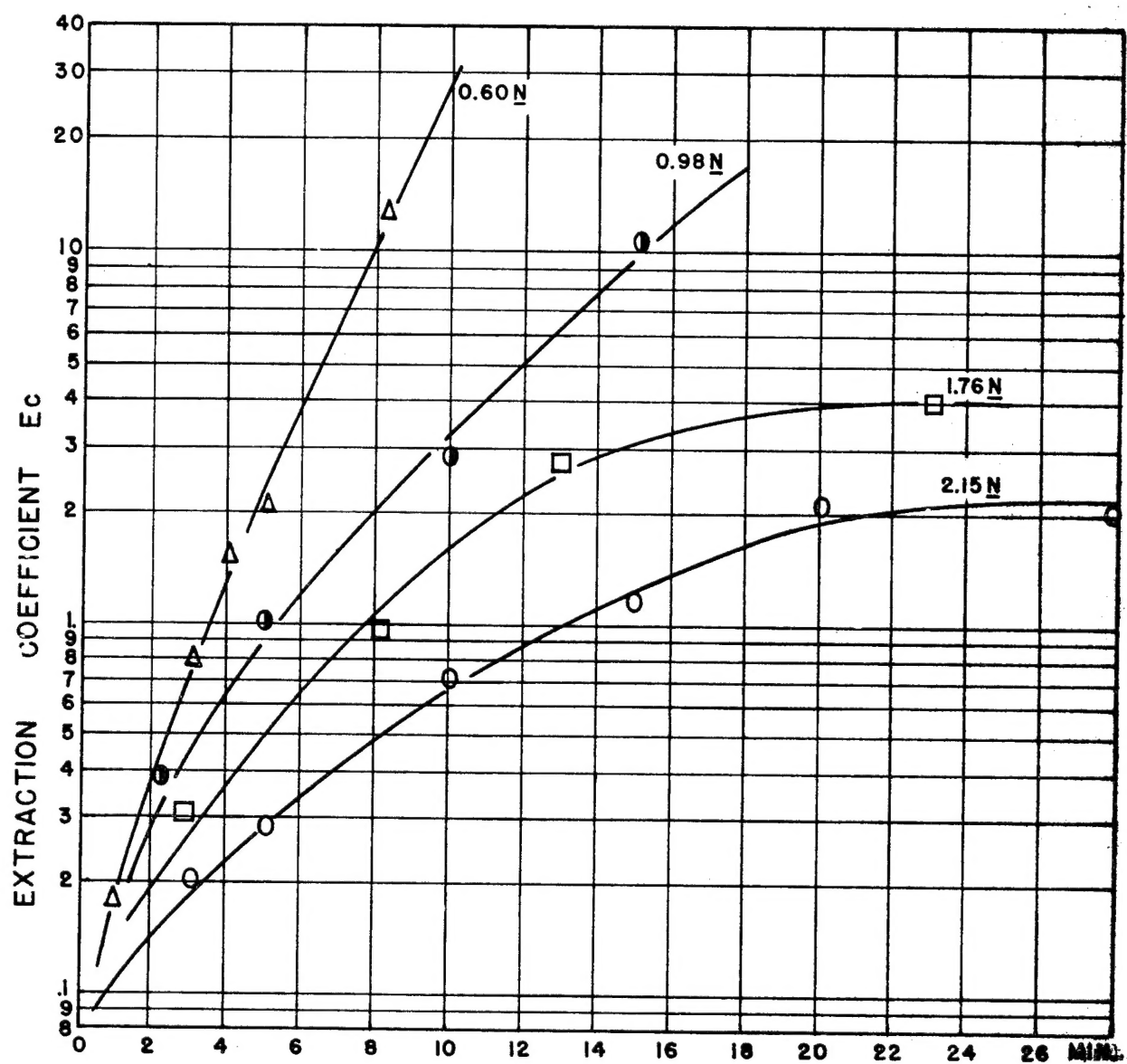—0.02 $\underline{M}$. TTA

—1.26 $\underline{N}$. HNO_3

FIGURE 18

ZIRCONIUM EXTRACTION RATE

0.00034 $\underline{M}$ Zr

− 0.02 $\underline{M}$. TTA.

DEPENDENCE ON HNO_3 CONCENTRATION
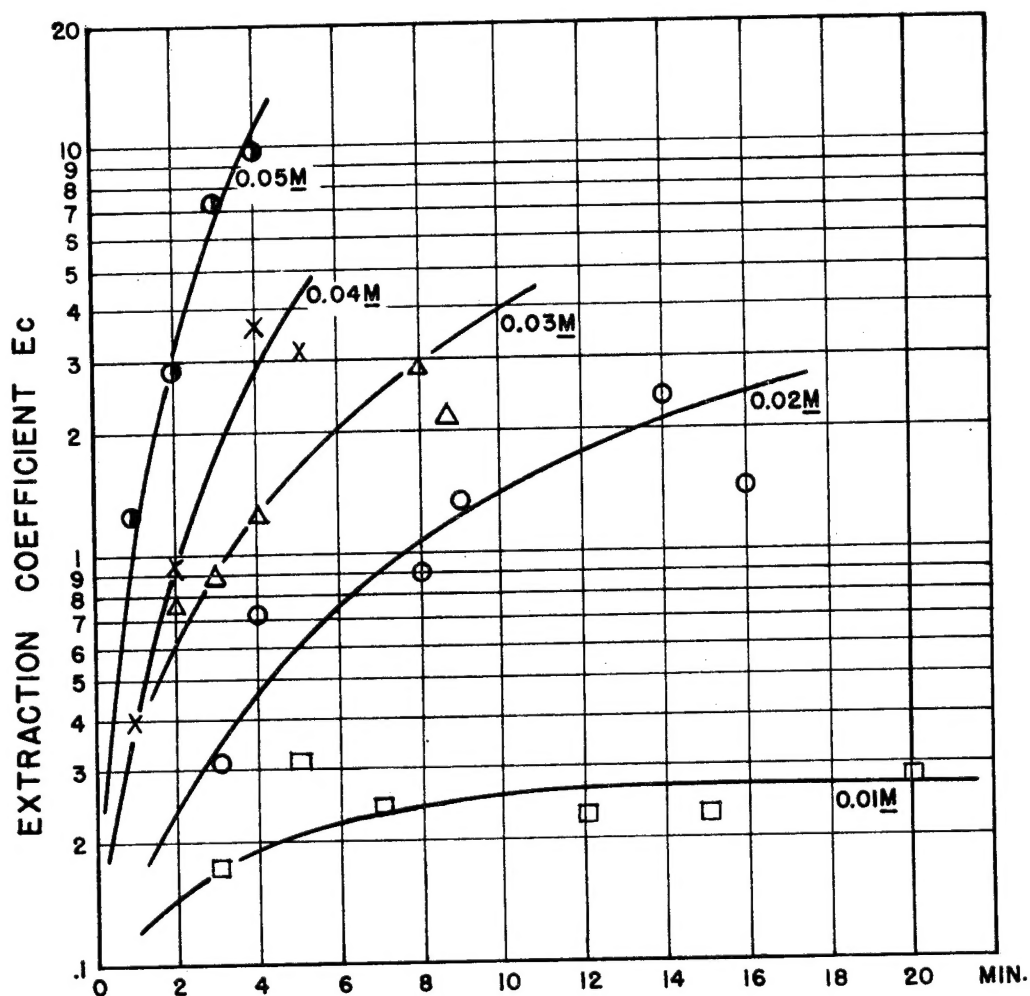
FIGURE 19

ZIRCONIUM EXTRACTION RATE

0.00015 $\underline{M}$ Zr

−2.03 $\underline{N}$ HNO$_3$

DEPENDENCE ON TTA CONCENTRATION